

REPORT 1112

HYDROCARBON AND NONHYDROCARBON DERIVATIVES OF CYCLOPROPANE

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SUMMARY

The methods used to prepare and purify 19 hydrocarbon derivatives of cyclopropane are discussed. Of these hydrocarbons, 13 were synthesized for the first time. In addition to the hydrocarbons, six cyclopropylcarbinols, five alkyl cyclopropyl ketones, three cyclopropyl chlorides, and one cyclopropanedicarboxylate were prepared as synthesis intermediates.

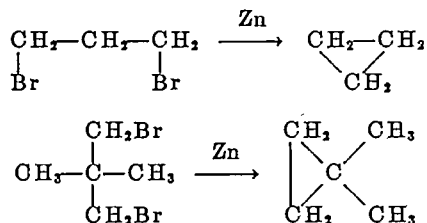
The melting points, boiling points, refractive indices, densities, and, in some instances, heats of combustion of both the hydrocarbon and nonhydrocarbon derivatives of cyclopropane were determined. These data and the infrared spectrum of each of the 34 cyclopropane compounds are presented herein.

The infrared absorption bands characteristic of the cyclopropyl ring are discussed, and some observations are made on the contribution of the cyclopropyl ring to the molecular refractions of cyclopropane compounds.

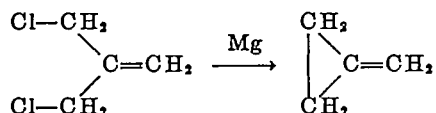
INTRODUCTION

The synthesis and purification of cyclopropane hydrocarbons was begun at the NACA Lewis laboratory in 1944 in order to provide high-purity samples of substituted cyclopropanes for an investigation of the effect of molecular structure on combustion characteristics and other properties pertinent to research on fuels for aircraft propulsion systems. The present report summarizes the research pertaining to the synthesis of 19 hydrocarbon and 15 nonhydrocarbon derivatives of cyclopropane.

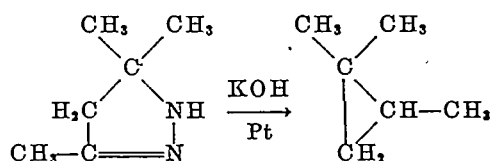
Few general methods for preparing hydrocarbons which contain the cyclopropyl ring are known. The method of Gustavson, which involves the reaction of α,γ -dibromides with zinc dust in a protonic solvent, has frequently been used (refs. 1 to 6):



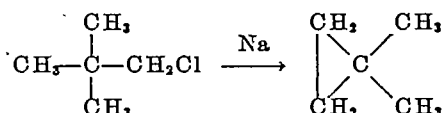
A modification of the Gustavson reaction, in which magnesium reacted in tetrahydrofuran with an α,γ -dichloride, was recently used to prepare methylenecyclopropane (ref. 7):



The pyrolysis of pyrazolines has also found limited use for the preparation of certain cyclopropanes (refs. 8 to 11):

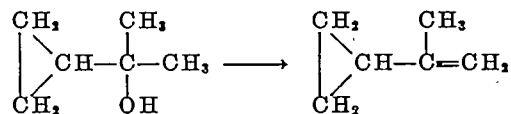


A method reported by Whitmore and co-workers (refs. 12 to 15) involves the removal of hydrogen halide from alkyl halides in which the halogen atom is one carbon removed from a quaternary carbon atom:

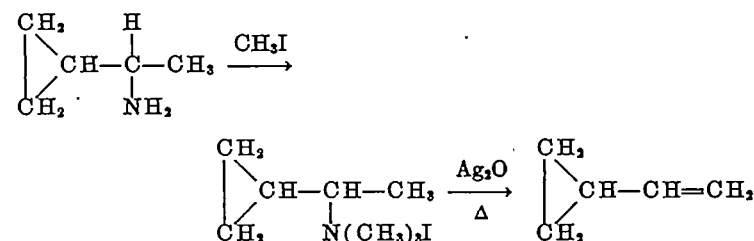


In each of these methods the cyclopropane ring is formed during the reaction.

Another approach to the synthesis of cyclopropane hydrocarbons is that which involves the conversion of nonhydrocarbon derivatives of cyclopropane to the corresponding hydrocarbon derivatives. For example, some of the carbinol derivatives of cyclopropane have been dehydrated with acidic catalysts to the corresponding cyclopropylalkenes (refs. 16 to 20):

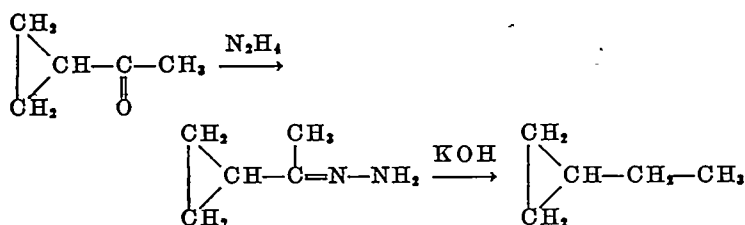


Exhaustive methylation of cyclopropylcarbinylamines also has been reported to yield cyclopropylalkenes (ref. 21):



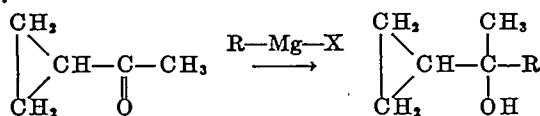
In an analogous manner, cyclopropene has been prepared from cyclopropylamine (ref. 22). For the preparation of

certain cyclopropylalkanes, the Wolff-Kishner reduction of cyclopropyl ketones has been used (refs. 23 to 25):



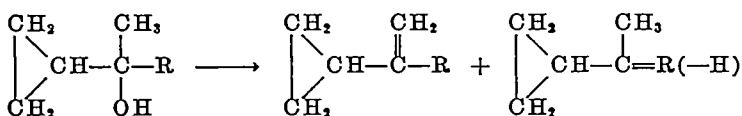
The usefulness of all the reactions described is limited by the availability of starting materials. With few exceptions, the α,γ -dibromides for the Gustavson reaction, the pyrazolines, the halides suitable for hydrogen halide elimination reactions, and the nonhydrocarbon derivatives of cyclopropane are not commercially available. Consequently, cyclopropane hydrocarbons generally have been prepared only in limited research quantities. With the exception of cyclopropane itself, which has been used as an anesthetic, none of the cyclopropane hydrocarbons are available commercially.

The announcement during World War II of the commercial availability of methyl cyclopropyl ketone coincided with the interest of the Lewis laboratory in the preparation of cyclopropane hydrocarbons. It was believed that this nonhydrocarbon derivative of cyclopropane could be used to prepare a series of cyclopropane hydrocarbons in the following manner: The ketone was known to react with Grignard reagents to give methylalkylcyclopropylcarbinols (refs. 26 and 27):

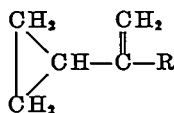


[R, hydrocarbon radical; X, halogen atom]

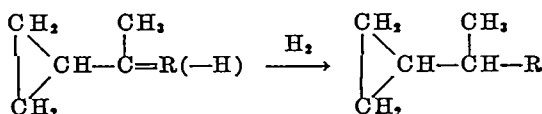
By using different R—X compounds for the preparation of R—Mg—X, the length and the degree of branching of the hydrocarbon chain could be varied. The methylalkylcyclopropylcarbinols were known to dehydrate in the presence of acid catalysts to the cyclopropylalkenes (refs. 16 to 20), although the practicability of the reaction as a synthesis method had not been established:



The selective hydrogenation of the cyclopropylalkenes to the corresponding cyclopropylalkanes had not been investigated; but it was believed that by proper selection of catalyst, temperature, and pressure, the desired hydrogenation could be accomplished:



or



(Concurrently with the present research, the authors of refs. 28 and 29 attempted the catalytic hydrogenation of 2-cyclopropylpropene and vinylcyclopropane. The catalyst and the reaction conditions employed by them yielded the corresponding cyclopropylalkanes but also gave considerable amounts of paraffinic hydrocarbons.)

A total of 12 cyclopropylalkenes and 5 cyclopropylalkanes were prepared in this manner from methyl cyclopropyl ketone:

By dehydration of alkylcyclopropylcarbinols.—

Vinylcyclopropane
2-Cyclopropylpropene
2-Cyclopropyl-1-butene
2-Cyclopropyl-1-pentene
2-Cyclopropyl-1-hexene
2-Cyclopropyl-3-methyl-1-butene
2-Cyclopropyl-2-butene (l. b.)
2-Cyclopropyl-2-butene (h. b.)
2-Cyclopropyl-2-pentene (l. b.)
2-Cyclopropyl-2-pentene (h. b.)
2-Cyclopropyl-2-hexene (l. b.)
2-Cyclopropyl-2-hexene (h. b.)

(The abbreviations l. b. and h. b. denote the low-boiling and the high-boiling geometrical isomers, respectively.)

By hydrogenation of cyclopropylalkenes.—

2-Cyclopropylpropene
2-Cyclopropylbutene
2-Cyclopropylpentene
2-Cyclopropylhexene
2-Cyclopropyl-3-methylbutene

Of these 17 hydrocarbons, 12 were prepared for the first time.

In addition to the hydrocarbons, six cyclopropylcarbinols were obtained as synthesis intermediates, and five cyclopropyl ketones were obtained from the ozonization of the 2-cyclopropyl-1-alkenes:

Cyclopropylcarbinols from Grignard reactions.—

Dimethylcyclopropylcarbinol
Methylethylcyclopropylcarbinol
Methylpropylcyclopropylcarbinol
Methylisopropylcyclopropylcarbinol
Methylbutylcyclopropylcarbinol

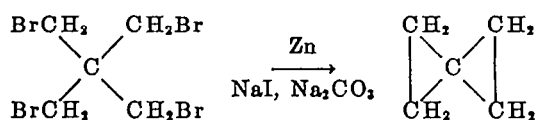
Cyclopropyl ketones from ozonization of 2-cyclopropyl-1-alkenes.—

Methyl cyclopropyl ketone
Ethyl cyclopropyl ketone
Propyl cyclopropyl ketone
Isopropyl cyclopropyl ketone
Butyl cyclopropyl ketone

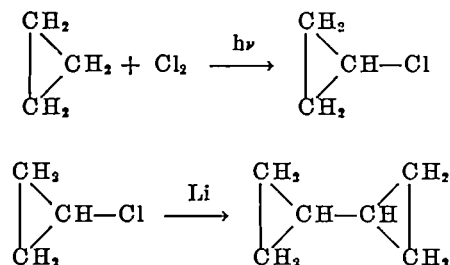
Cyclopropylcarbinol from reduction of cyclopropyl ketone.—

Methylcyclopropylcarbinol

Two other cyclopropane hydrocarbons, spiropentane and the smallest of the dicyclic hydrocarbons, dicyclopentyl, were prepared in the present investigation. Spiropentane was obtained from the debromination of pentaerythrityl tetrabromide, which was accomplished in a manner similar to that described by Hass and co-workers for preparing cyclopropane (ref. 30):



The preparation of dicyclopropyl involved the photochemical chlorination of cyclopropane (ref. 31) and the reaction of one of the chlorination products, cyclopropyl chloride, with lithium in ether:



From the photochemical chlorination of cyclopropane, two other cyclopropyl chlorides were isolated, namely, 1,1-dichlorocyclopropane and *trans*-1,2-dichlorocyclopropane.

Melting points, boiling points, refractive indices, densities, and, in some instances, heats of combustion of the hydrocarbon and nonhydrocarbon derivatives of cyclopropane which were either prepared for the first time or isolated in a higher state of purity than heretofore were determined. The infrared spectra of the 34 cyclopropane compounds were also determined, and each of the spectra is presented herein. Some observations on the molecular refraction of cyclopropane compounds are included in the report.

APPARATUS

The Grignard reactions were carried out in either a 10- or a 30-gallon glass-lined reactor which was double-walled so that the reaction temperatures could be controlled by passing steam or cold or hot water between the inner and outer walls. The reactors were equipped with efficient motor-driven stirrers, high-capacity reflux condensers, and stainless steel tanks from which liquid reactants were fed by gravity into the reactors.

The column used in dehydrating some of the cyclopropylcarbinols consisted of a 2.5- by 90-centimeter pyrex tube which was filled with 8 to 14 mesh alumina and heated by resistance-element tube furnaces. Temperatures of the furnaces were controlled by manual adjustment of variable transformers between the furnaces and the laboratory power supply. Column temperatures were read from an indicating potentiometer connected to thermocouples which were held in place against the outer walls of the pyrex dehydration tube by means of copper strips. A bellows-type pump was used to force the liquid carbinols into the top of the column; the vaporized products issuing from the bottom of the column were condensed by a water-cooled spiral condenser and collected in a flask at room temperature. The flask in turn was connected to a trap chilled with solid carbon dioxide and acetone, so that products volatile at room temperature

could also be collected. A sketch of the assembly is shown in figure 1.

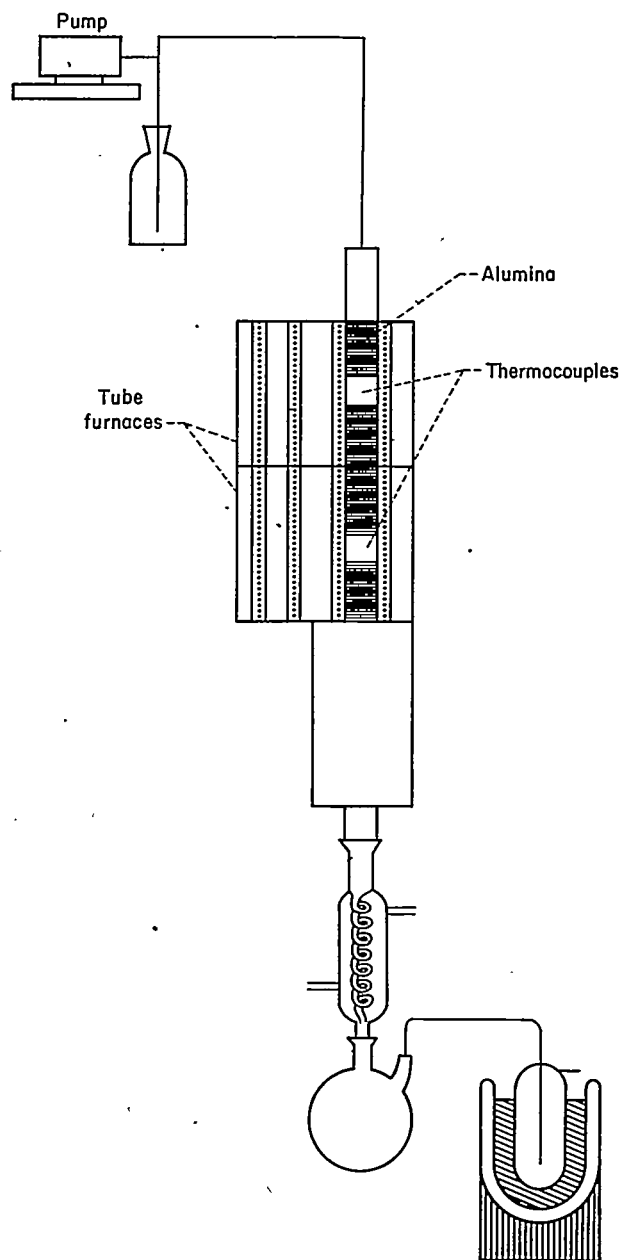


FIGURE 1.—Apparatus used in dehydrating cyclopropylcarbinols over alumina.

The hydrogenation reactions were conducted in high-pressure steel autoclaves of 1-, 3.4-, and 4.4-liter capacities. The autoclaves were equipped with rocker-type shaking mechanisms, resistance heaters, thermocouples and potentiometers for determining reaction temperatures, and appropriate valves, pressure gages, and high-pressure lines for introducing hydrogen into the vessels.

Fractional distillation columns were used in the purification of intermediates and final products. For fractionations at reduced pressures, 2.5- by 180-centimeter pyrex columns, which were packed with $\frac{3}{16}$ -inch single-turn glass helices, were used. Columns 2.2 by 180 centimeters, packed with $\frac{1}{8}$ -inch single-turn glass helices, were used for fractionations of those intermediates which could be distilled at atmospheric pressure and for the initial fractionations of the hydrocarbons.

For final purification of the hydrocarbons, 2.5- by 180 centimeter Podbielniak columns, operated at efficiencies in excess of 150 theoretical plates, were employed.

The ozonization apparatus, used in the identification of cyclopropylalkenes, was similar to that described in reference 32. A 0.25 kilovolt-ampere transformer with an input of 120 volts and an output of 25,000 volts was used to supply the necessary potential to the electrodes of the ozonizer tube.

The apparatus for the photochemical chlorination of cyclopropane was essentially the same as that described in reference 31 except that the recycling system was eliminated. The reactor was constructed of 0.7-centimeter pyrex tubing which was bent to form a planar grid; total length of the tubing was 470 centimeters. The reactor was illuminated by two G. E. type-RS sun lamps placed directly in front of the grid and mounted so that their distance from the grid could be varied. The scrubbing towers for removing the hydrogen chloride and the chlorine from the reaction products were constructed of 0.45- by 122-centimeter pyrex tubing and were packed with $\frac{1}{4}$ -inch Berl saddles to increase the contact area. The flowmeters in the system were used primarily to check the constancy of gas flows; quantities of reactants were measured by loss in weight of the gas cylinders. A sketch of the apparatus is shown in figure 2.

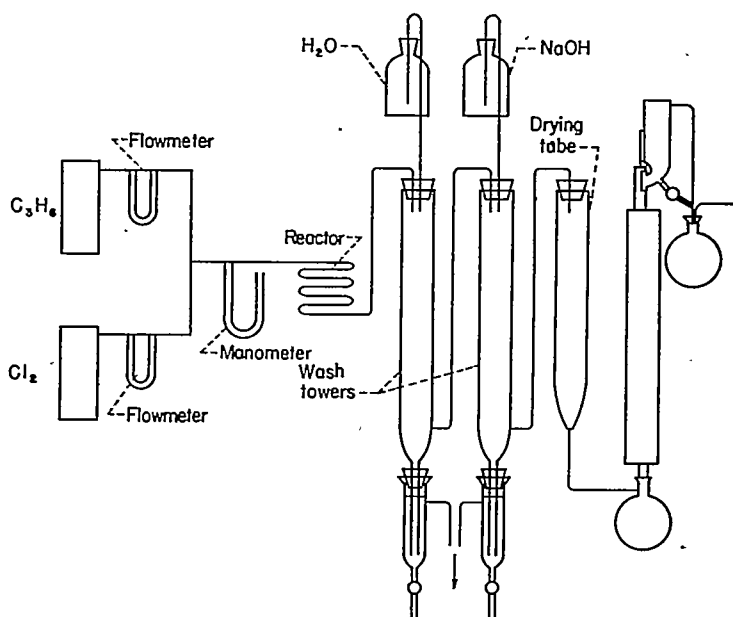


FIGURE 2.—Apparatus used for photochlorination of cyclopropane.

The infrared spectrophotometer used in determining the infrared spectra of the hydrocarbon and nonhydrocarbon derivatives of cyclopropane was a Baird Associates double-beam recording spectrophotometer equipped with a sodium chloride prism. Liquid sample cells of 0.1-millimeter thickness were used, and the spectra of undiluted samples and also of samples diluted with either carbon tetrachloride or carbon disulfide were obtained.

DISCUSSION OF SYNTHESSES

Descriptions of the syntheses have been generalized in the following discussion; for detailed descriptions of each syn-

thesis, the reader is referred to the synthesis reports previously published (refs. 33 to 39).

ALKYLCYCLOPROPYLCARBINOLS

Methylcyclopropylcarbinol.—Five-mole quantities of methyl cyclopropyl ketone were reduced by four methods: (1) with sodium metal in 75-percent ethyl alcohol, (2) with lithium aluminum hydride in ether, (3) with hydrogen in the presence of Raney nickel catalyst, and (4) with hydrogen in the presence of copper chromite catalyst. The reactions and products are summarized in the following table (ref. 33):

Reducing agent	Moles of reducing agent	Reaction temperature, °C	Moles of ketone recovered	Yield of carbinol, percent	Yield of pentanol-2, percent
Na and aqueous alcohol	14	10-15	None	42	0
LiAlH ₄	2	35-45	None	76	0
H ₂ -Raney Ni	Theoretical	90-125	0.55	34	30
H ₂ -copper chromite	do	100	None	90	0
Do	do	120	None	87	0
Do	do	150	None	70	ca. 10

These data show that of the methods investigated, the hydrogenation of methyl cyclopropyl ketone in the presence of copper chromite catalyst was the most satisfactory for preparing methylcyclopropylcarbinol. The reduction with lithium aluminum hydride was also acceptable for preparing small quantities of the carbinol, although the yields were not so high as those obtained catalytically with copper chromite. Neither the reduction with sodium nor that with Raney nickel was satisfactory because of the low yields of carbinol obtained and also, in the latter method, because of the formation of a close-boiling impurity, pentanol-2.

Methylalkylcyclopropylcarbinols.—The methylalkylcyclopropylcarbinols were prepared in ether by the reaction of methyl cyclopropyl ketone with the Grignard reagents of appropriate alkyl halides. In general, the Grignard reagent was prepared (in 2 to 5 percent excess) by adding the alkyl halide to a suspension of magnesium metal in ether, then adding the ketone to the Grignard reagent, and finally hydrolyzing the products of the reaction with saturated aqueous ammonium chloride solution. The quantities of reactants and the yields of the carbinols are summarized in the following table:

Alkyl halide	Moles of ketone	Cyclopropylcarbinol	Yield, percent	Reference
Methyl chloride	150	Dimethyl	64	34
Ethyl bromide	20	Methylethyl	77	34
Propyl bromide	150	Methylpropyl	51	34
Butyl bromide	97	Methylbutyl	52	34
Isopropyl bromide	120	Methylisopropyl	51	35

Because no attempt was made to determine the reaction conditions necessary for optimum yields of the carbinols, any relations existing between yields of the carbinols and their structures could not be deduced.

Halogenated impurities were found in all the carbinols. It has been suggested (ref. 28) that the use of an excess of ammonium chloride in the hydrolysis of the Grignard product is responsible for the halogenated impurities.

Although ammonium chloride may affect the extent of the side reaction which yields the halogenated impurities, a simple metathesis of the carbinols and the ammonium chloride does not appear to be the source of the impurities. For example, in the preparation of methylethylcyclopropyl-

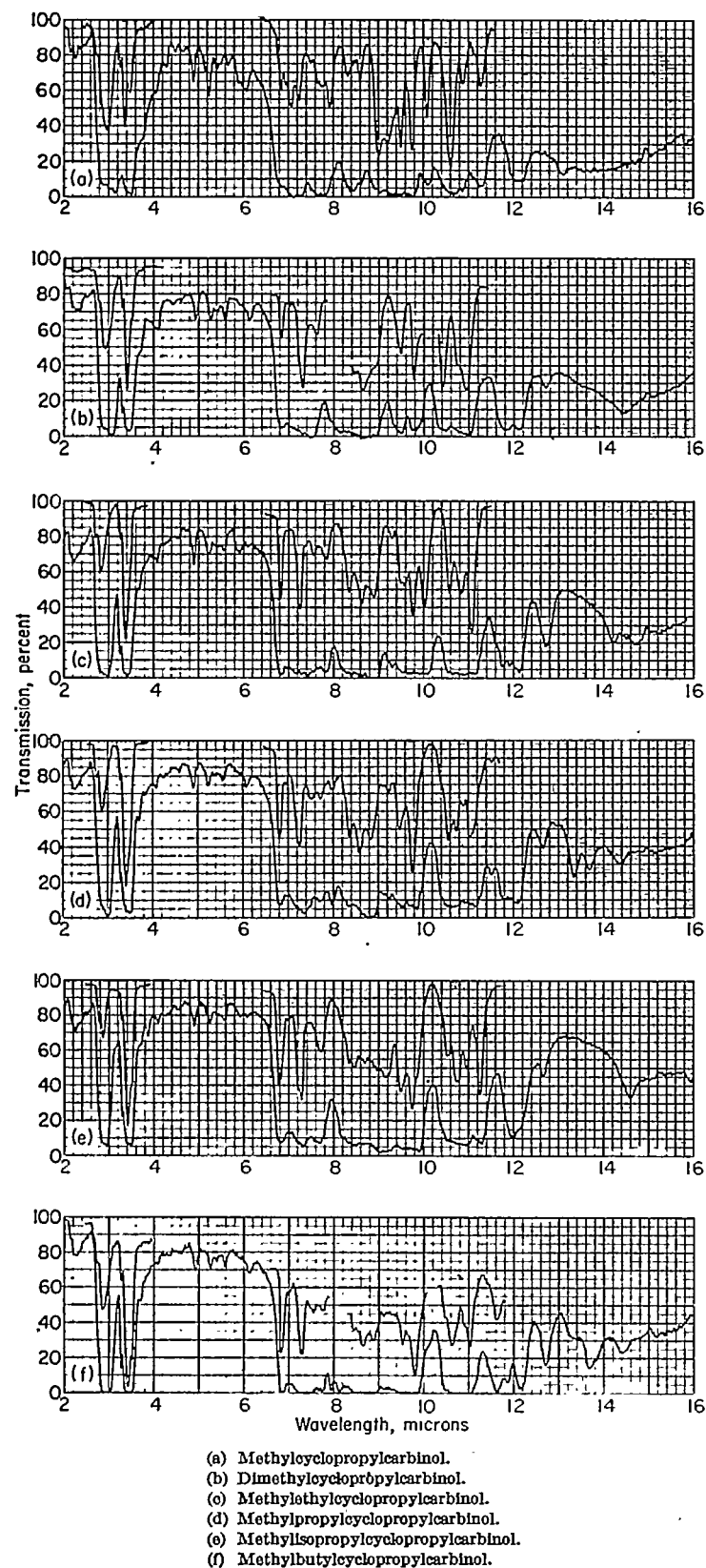


FIGURE 3.—Infrared spectra of cyclopropylcarbinols. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

carbinol, the halogenated impurity was isolated and the elemental analysis of it corresponded not to a chloride, but to a bromide, $C_7H_{13}Br$. The infrared spectrum of the impurity indicated the basic structure to be that of a type IV olefin ($R,R'C=CHR''$) rather than a cyclopropane derivative. The impurity was presumed to be 1-bromo-4-methyl-3-hexene; a similar structure was obtained when dimethylcyclopropylcarbinol was treated with hydrogen halide (ref. 40). The halogenated impurities were removed from the carbinols by refluxing them with alcoholic sodium hydroxide, removing the precipitated sodium halide by extraction with water, and fractionating the carbinol at reduced pressure.

The physical properties of the cyclopropylcarbinols are compared in the following table with those properties previously reported:

Cyclopropylcarbinol	Melting point, °C	Boiling point, °C	n_D^{20}	d_4^{20} , g/ml	Reference
Methyl-----	-31.04	122.5	1.4316	0.8886	33
Literature-----	-32.1	123.5	1.4316	.8893	29
Dimethyl-----	(*)	123.7	1.4335	.8789	34
Literature-----	-43.0	123.4	1.4337	.8842	28
Methylethyl-----	(*)	142.3	1.4412	.8807	34
Literature-----	-----	143.4-143.8 (776 mm)	1.44163	.88565	26
Methylpropyl-----	(*)	163.5	1.4438	.8763	34
Literature-----	-----	163.5-163.9 (761 mm)	1.44344	.87721	26
Methylbutyl-----	(*)	183.7	1.4466	.8735	34
Literature-----	-----	182-183 (752 mm)	1.44514	.87447	26
Methylisopropyl-----	(*)	160.3	1.4465	.8856	35

* Pressure, 760 mm Hg unless otherwise noted.

† Equilibrium melting curves could not be obtained.

‡ Formed glasses.

The infrared spectra of the cyclopropylcarbinols are shown in figure 3; characteristic absorption for the hydroxyl group is observed between 2.8 and 3.0 microns and for the cyclopropyl group, between 9.75 and 9.80 microns.

CYCLOPROPYLALKENES

The cyclopropylalkenes were prepared by dehydrating the appropriate alkyl- or methylalkylcyclopropylcarbinols. Two methods of dehydrating the carbinols were investigated:

Alumina.—The carbinol (in some cases dissolved in toluene) was passed at a rate of 5 to 10 milliliters per minute through a 2.5- by 120-centimeter pyrex tube which was packed with 8 to 14 mesh alumina and heated to between 200° and 300° C. A sketch of the apparatus is shown in figure 1.

The yields of products and the reaction conditions for the dehydration of methylcyclopropylcarbinol are summarized in the following table (ref. 36):

Column temperature, °C	Rate, ml/min	Yield of products, percent				
		Propene	Isoprene	Vinylcyclopropane	1,3-Pentadienes	2-Methyltetrahydrofuran
265-280-----	10	1	1	52	2	4
285-300-----	10	4	3	54	5	4
285-300-----	5	6	3	38	8	3

In each of these experiments the carbinol was dissolved in an approximately equal volume of toluene, and the solution was passed through the dehydration column.

It can be seen from the data presented in the table that although increasing the temperature from the range 265° to 280° C to the range 285° to 300° C increased the yields of products to some extent, the change in rate of introducing the solution of carbinol into the dehydration column had a much greater effect on the yields of products. At the lower rate the yield of vinylcyclopropane was significantly reduced, and the yields of other products except the tetrahydrofuran and isoprene were increased. The decomposition and isomerization of vinylcyclopropane in the presence of alumina has not been investigated; therefore, it is not known whether the increase in the yields of propene and 1,3-pentadienes at the lower rate is caused by decomposition and isomerization of vinylcyclopropane or by isomerization of the methylecyclopropylcarbinol and subsequent dehydration of the resultant carbinol.

Several methylalkylcyclopropylcarbinols were also dehydrated by passing the pure carbinol or, in the case of dimethylcyclopropylcarbinol, a toluene solution of the carbinol, over alumina at a rate of 5 milliliters per minute and at temperatures between 200° and 250° C. With the exception of dimethylcyclopropylcarbinol, the dehydration of all

the methylalkylcyclopropylcarbinols investigated gave mixtures of 2-cyclopropyl-1- and 2-alkenes. Dimethylcyclopropylcarbinol gave in addition to 2-cyclopropylpropene small amounts of methylpentadienes and 2,2-dimethyltetrahydrofuran. The yields of 2-cyclopropylalkenes from each of the carbinols are given in the following table:

Cyclopropyl-carbinol	Column temperature, °C	Cyclopropyl-1-alkene	Yield, percent	Cyclopropyl-2-alkene	Yield, percent	Reference
Dimethyl.....	200-250	2-Cyclopropylpropene.	57	-----	-----	34
Methylethyl...	200-250	2-Cyclopropyl-1-butene.	32	2-Cyclopropyl-2-butene.	47	34
Methylpropyl...	225-250	2-Cyclopropyl-1-pentene.	39	2-Cyclopropyl-2-pentene.	38	34
Methylbutyl...	225-250	2-Cyclopropyl-1-hexene.	41	2-Cyclopropyl-2-hexene.	37	34
Methylisopropyl-	200-250	2-Cyclopropyl-3-methyl-1-butene.	64	2-Cyclopropyl-3-methyl-2-butene.	0	35

These data indicate that in general the yields of the 2-cyclopropyl-1-alkenes increase as the length of the alkyl chain increases, while the yields of the 2-cyclopropyl-2-alkenes decrease. The presence of branching at the carbon adjacent to the hydroxyl group also increases the yield of the 1-alkene and decreases the yield of the 2-alkene.

Sulfuric acid.—In the dehydrations of the methylalkylcyclopropylcarbinols with concentrated sulfuric acid, 6 to 10 moles of the carbinol with 0.4 to 0.8 milliliters of acid was heated to reflux in a flask attached to a 2.2- by 160-centimeter fractionating column which was packed with 1/8-inch glass helices. The dehydration products were removed through a distilling head at the top of the column as they formed. The only products obtained by this method were the 2-cyclopropyl-1- and 2-alkenes. The quantities of reactants and the yields of products are summarized in the following table (ref. 34):

Cyclopropyl-carbinol	Carbinol, moles	Acid, ml	2-Cyclopropyl-1-alkene	Yield, percent	2-Cyclopropyl-2-alkene	Yield, percent
Dimethyl.....	6	0.4	-propene...	69	-----	-----
Methylethyl...	8	.8	-butene...	23	-butene...	50
Methylpropyl...	10	.4	-pentene...	19	-pentene...	50
Methylbutyl...	10	.8	-hexene...	21	-hexene...	57

From these data the length of the alkyl chain does not appear to have a significant effect on the yields of the 2-cyclopropyl-1- and 2-alkenes.

A dependence of the yields of products on the method of dehydrating the methylalkylcyclopropylcarbinols is illustrated by the distillation data presented in figure 4. In the case of dimethylcyclopropylcarbinol, the dehydration with sulfuric acid yielded only the 2-cyclopropylpropene, whereas the dehydration with alumina also gave small quantities of a product of higher refractive index (probably methylpentadienes) and a product of lower refractive index (2,2-dimethyltetrahydrofuran). In the case of the other carbinols, the dehydration with sulfuric acid did not give so large a proportion of the 2-cyclopropyl-1-alkene as did the dehydration with alumina.

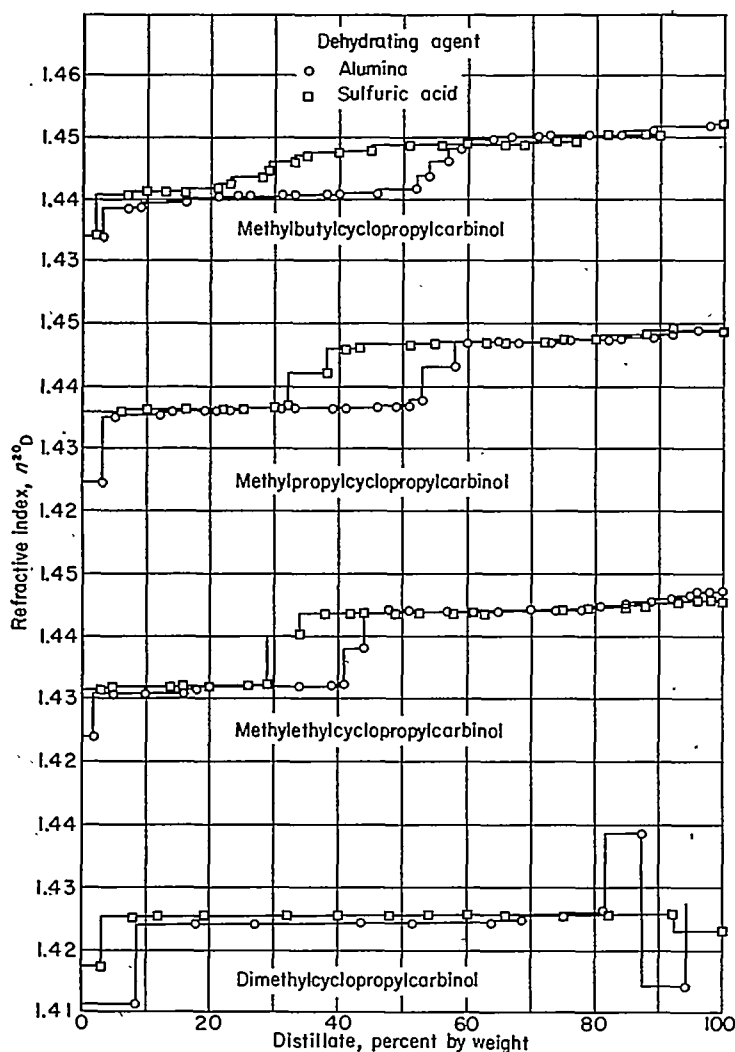


FIGURE 4.—Distillation of products from dehydration of methylalkylcyclopropylcarbinols.

Distillation data are also presented for the products from the dehydration of methylcyclopropylcarbinol (fig. 5) and for the dehydration of methylisopropylcyclopropylcarbinol (fig. 6) with alumina. From methylcyclopropylcarbinol, propene and isoprene were obtained at the beginning of the fractionation and 1,3-pentadienes and 2-methyltetrahydrofuran at the end of the fractionation. From methylisopropylcyclopropylcarbinol, only the 1-alkene (2-cyclopropyl-3-methyl-1-butene) and a high-boiling residue were obtained.

With the exception of 2-cyclopropylpropene and 2-cyclopropyl-3-methyl-1-butene, the cyclopropylalkenes were purified by azeotropic fractionations with appropriate entrainers in the Podbielniak columns after preliminary fractionations at efficiencies of 50 to 60 theoretical plates. Azeotropic fractionation was found to be necessary in order to separate geometrical isomers and close-boiling impurities from the cyclopropylalkenes. In the following table pertinent physical properties of the hydrocarbons, the entrainers, and the azeotropes are given:

Cyclopropylalkene	n_D^{20}	Entrainer	n_D^{20}	Azeotrope	
				n_D^{20}	Boiling point, °C
Vinylcyclopropane.....	1.4138	Ethanol.....	1.3614	1.4105	39
2-Cyclopropyl-1-butene.....	1.4319	do.....	1.3614	1.3975	73
2-Cyclopropyl-2-butene (l. b.).....	1.4428	do.....	1.3614	1.3950	75
2-Cyclopropyl-2-butene (h. b.).....	1.4474	do.....	1.3614	1.3957	76
2-Cyclopropyl-1-pentene.....	1.4362	Propanol.....	1.3854	1.4036	95
2-Cyclopropyl-2-pentene (l. b.).....	1.4458	do.....	1.3854	1.4029	96
2-Cyclopropyl-2-pentene (h. b.).....	1.4502	do.....	1.3854	1.4023	96
2-Cyclopropyl-1-hexene.....	1.4403	Cellosolve.....	1.4079	1.4215	131
2-Cyclopropyl-2-hexene (l. b.).....	1.4486	do.....	1.4079	1.4239	132
2-Cyclopropyl-2-hexene (h. b.).....	1.4529	do.....	1.4079	1.4249	132

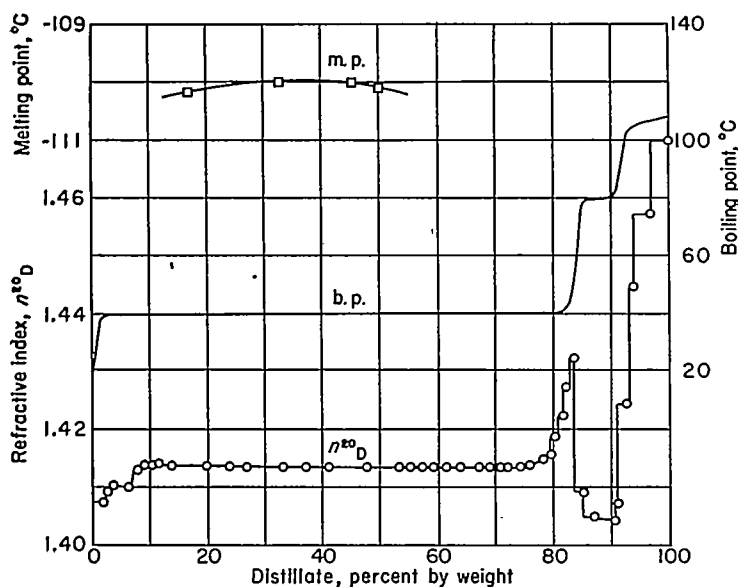


FIGURE 5.—Distillation of products from dehydration of methylcyclopropylcarbinol over alumina at 265° to 280° C.

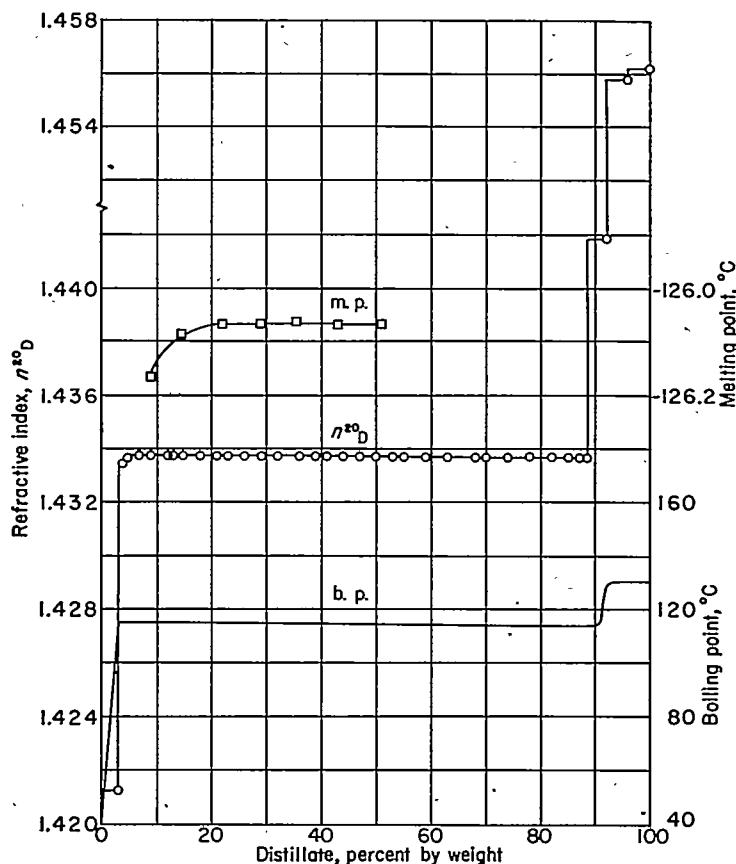


FIGURE 6.—Distillation of products from dehydration of methylisopropylcyclopropylcarbinol over alumina. Distillate, 1120 grams.

The physical properties of the cyclopropylalkenes are given in the following table. In those instances in which the compound has been previously reported, reference is made to the properties obtained by other investigators.

Cyclopropylalkene	Melting point, °C	Boiling point, °C	n_D^{20}	d_4^{20} , g/ml	Net heat of combustion, kcal/mole
Vinylcyclopropane.....	-109.82	40.19	1.4138	0.72105	720
Ref. 29.....	-112.6	40.41	1.4156	.7160	-----
Ref. 21.....	-----	40.0-40.2 (755 mm)	1.4172	.723 (18°C)	-----
2-Cyclopropylpropene..	-102.34	70.33	1.4255	.75153	875
Ref. 28.....	-102.36	70.41	1.4254	.7514	-----
Ref. 20.....	-----	69.5-70.0 (751 mm)	1.42524	.74999	-----
2-Cyclopropyl-1-butene.	^b -119.55	98.57	1.4319	.76820	1,025
Ref. 20.....	-121.94	-----	-----	-----	-----
2-Cyclopropyl-2-butene (l. b.).....	-97.83	103.5-103.8	1.43901	.7772	1,020
2-Cyclopropyl-2-butene (h. b.).....	-74.07	106.55	1.4428	.78100	-----
Ref. 20.....	-----	107.46	1.4474	.78745	-----
2-Cyclopropyl-1-pentene.	-113.87	105.5-106	1.44253	.7804	1,165
2-Cyclopropyl-2-pentene (l. b.).....	-113.65	123.94	1.4362	.77660	-----
2-Cyclopropyl-2-pentene (h. b.).....	-107.61	128.61	1.4458	.78402	1,165
2-Cyclopropyl-1-hexene.	-106.16	129.98	1.4502	.79077	-----
2-Cyclopropyl-2-hexene (l. b.).....	-----	148.89	1.4403	.78447	1,320
2-Cyclopropyl-2-hexene (h. b.).....	Glass	162.08	1.4486	.79051	-----
2-Cyclopropyl-3-methyl-1-butene	-97.40	163.08	1.4529	.79666	1,305
Ref. 20.....	-126.06	116.81	1.4337	.77395	1,160

*Pressure, 760 mm Hg unless otherwise stated.

^bTwo crystalline modifications were observed.

The estimated melting points for zero impurity, the depressions in melting points per mole percent of added impurity, and the calculated purities of some of the cyclopropylalkenes are given in the following table:

Hydrocarbon	Observed melting point, °C	Estimated melting point for zero impurity, °C	Change in melting point per mole percent of added impurity, °C	Calculated purity, mole percent
Vinylcyclopropane.....	-109.82	-109.81	b 0.28	99.9
2-Cyclopropylpropene.....	-102.34	-102.33	c. 25	99.9
2-Cyclopropyl-1-butene.....	-119.55	-119.50	-----	-----
2-Cyclopropyl-2-butene (l. b.).....	-97.83	-97.62	-----	-----
2-Cyclopropyl-2-butene (h. b.).....	-74.07	-74.03	-----	-----
2-Cyclopropyl-1-pentene.....	-113.87	-113.83	-----	-----
2-Cyclopropyl-2-pentene (l. b.).....	-113.65	-113.55	-----	-----
2-Cyclopropyl-2-pentene (h. b.).....	-107.61	-107.43	-----	-----
2-Cyclopropyl-3-methyl-1-butene.....	-128.06	-125.98	-----	-----
2-Cyclopropyl-1-hexene.....	-106.16	-106.09	-----	-----

a Determined by the geometrical construction of reference 41.

b Determined by adding known amounts of 1-*trans*-3-pentadiene.

c Value taken from reference 28.

Although the purities of only the first two cyclopropylalkenes were calculated, it is believed that the purities of the others listed in the table are better than 99 mole percent, because the differences in the estimated melting points for zero impurity and the observed melting points are small. The geometrical isomers of 2-cyclopropyl-2-hexene are not included in the table, because the lower-boiling isomer could not be crystallized and the melting curve of the higher-boiling isomer was not of sufficient duration to make a reliable estimate of the melting point for zero impurity.

The infrared spectra of the cyclopropylalkenes from 2 to 16 microns are shown in figure 7. It can be seen that for those molecules having a terminal C=C, the absorption for the double-bond stretching frequencies occurs at 6.1 ± 0.02 microns; whereas for those molecules having an internal C=C, the absorption occurs at a lower wavelength, 6.02 ± 0.02 microns. The intensity of the absorption is much greater for the terminal double bond than for the internal double bond. Characteristic absorption for the cyclopropyl ring occurs at 9.78 microns in those molecules having a terminal double bond; in those molecules having an internal double bond the absorption for the cyclopropyl ring occurs at a slightly higher wavelength, 9.81 microns.

ALKYL CYCLOPROPYL KETONES

The alkyl cyclopropyl ketones were obtained as fragmentation products from the ozonolysis of the 2-cyclopropyl-1-alkenes. The methods of ozonolysis and hydrogenation of the ozonide have been described in reference 32. In general, the olefin was dissolved in 100 to 150 milliliters of absolute alcohol and an oxygen-ozone mixture containing from 5 to 10 percent ozone was passed through the solution until all the olefin had been converted to ozonide. The ozonide solution was then transferred to a low-pressure hydrogenation apparatus, and the ozonide decomposed with hydrogen in the presence of a palladium catalyst to give the alkyl cyclopropyl ketone and formaldehyde. The alkyl cyclopropyl ketones were identified by their physical properties and by analysis of their 2, 4-dinitrophenylhydrazone derivatives. The quantities of olefin used, the yields of the alkyl cyclopropyl ketones,

and the melting points of the 2,4-dinitrophenylhydrazone derivatives are given in the following table:

2-Cyclopropyl-1-alkene *	Olefin, moles	Alkyl cyclopropyl ketone	Yield, percent	Melting point of 2,4-dinitrophenylhydrazone, °C	Reference
-propene.....	0.3	Methyl.....	(b)	148.6-149.2	34
-butene.....	.28	Ethyl.....	39	160.4-160.5	34
-pentene.....	.48	Propyl.....	43	165.0-165.5	34
-hexene.....	.3	Butyl.....	75	114.5-115.0	34
-3-methyl-1-butene.....	.3	Isopropyl.....	42	187.5-188.0	35

* The structures of the 2-cyclopropyl-2-alkenes were also proved by ozonolysis; only those alkenes yielding cyclopropyl ketones are listed here.

b Paraformaldehyde sublimed at the boiling temperature of the ketone making it difficult to determine the yield of the ketone.

The infrared spectra of the alkyl cyclopropyl ketones are shown in figure 8. All show strong absorption at 5.9 microns, which is characteristic of the carbonyl group. With the exception of methyl cyclopropyl ketone, all show characteristic absorption for the cyclopropyl ring between 9.75 and 9.80 microns; cyclopropyl ring absorption in methyl cyclopropyl ketone occurs at a lower wavelength, 9.69 microns.

2-CYCLOPROPYLALKANES

The 2-cyclopropylalkanes were prepared by hydrogenating the 2-cyclopropyl-1- and -2-alkenes in the presence of a barium-promoted copper chromite catalyst. The 1-alkenes and 2-alkenes were hydrogenated separately, because the position of the double bond was found to affect the ease of hydrogenation and the yields of products. In general, the olefin, an equal volume of ethanol, and a quantity of the catalyst equal to 10 percent of the weight of the olefin were put into the hydrogenator, and hydrogen was admitted to between 1500 and 1800 pounds per square inch gage. The hydrogenator rocking mechanism and the resistance heaters were turned on, and the vessel was heated to 100° C. The 2-cyclopropyl-1-alkenes hydrogenated readily at this temperature, the heat of reaction generally raising the temperature to between 120° and 130° C. The 2-cyclopropyl-2-alkenes hydrogenated sluggishly even at 130° C, and, in some instances, the reaction temperature was increased to as high as 175° C in order to obtain more rapid hydrogenation. The reaction conditions and the yields of products are summarized in the following table:

Olefin	Reaction conditions		Estimated composition of products				
2-Cyclopropylalkene	Temperature, °C	Initial H ₂ pressure, lb/sq in. gage	2-Cyclopropylalkane	Weight, percent	Methylalkane	Weight, percent	Reference
-propene.....	100-130	1,500	-propane...	98	2-Methylpentane	2	37
-1-butene.....	100-130	1,600	-butane.....	99	3-Methylhexane	1	37
-2-butene.....	110-130	1,500do.....	72do.....	15	37
-1-pentene.....	100-110	1,500	-pentane.....	99	4-Methylheptane	1	37
-2-pentene.....	120-130	1,750do.....	71do.....	17	37
-1-hexene.....	100-120	1,500	-hexane.....	99	4-Methyloctane	1	37
-2-hexene.....	150-175	1,500do.....	79do.....	10	37
-3-methyl-1-butene	100-140	1,850	-3-methylbutane.	99	2,3-Dimethylhexane.	1	35

* Unhydrogenated olefin was found in the product from each of the 2-alkenes.

These data and the distillation curves shown in figure 9 indicate that the hydrogenation of the 2-cyclopropyl-1-alkenes yields the corresponding 2-cyclopropylalkanes in

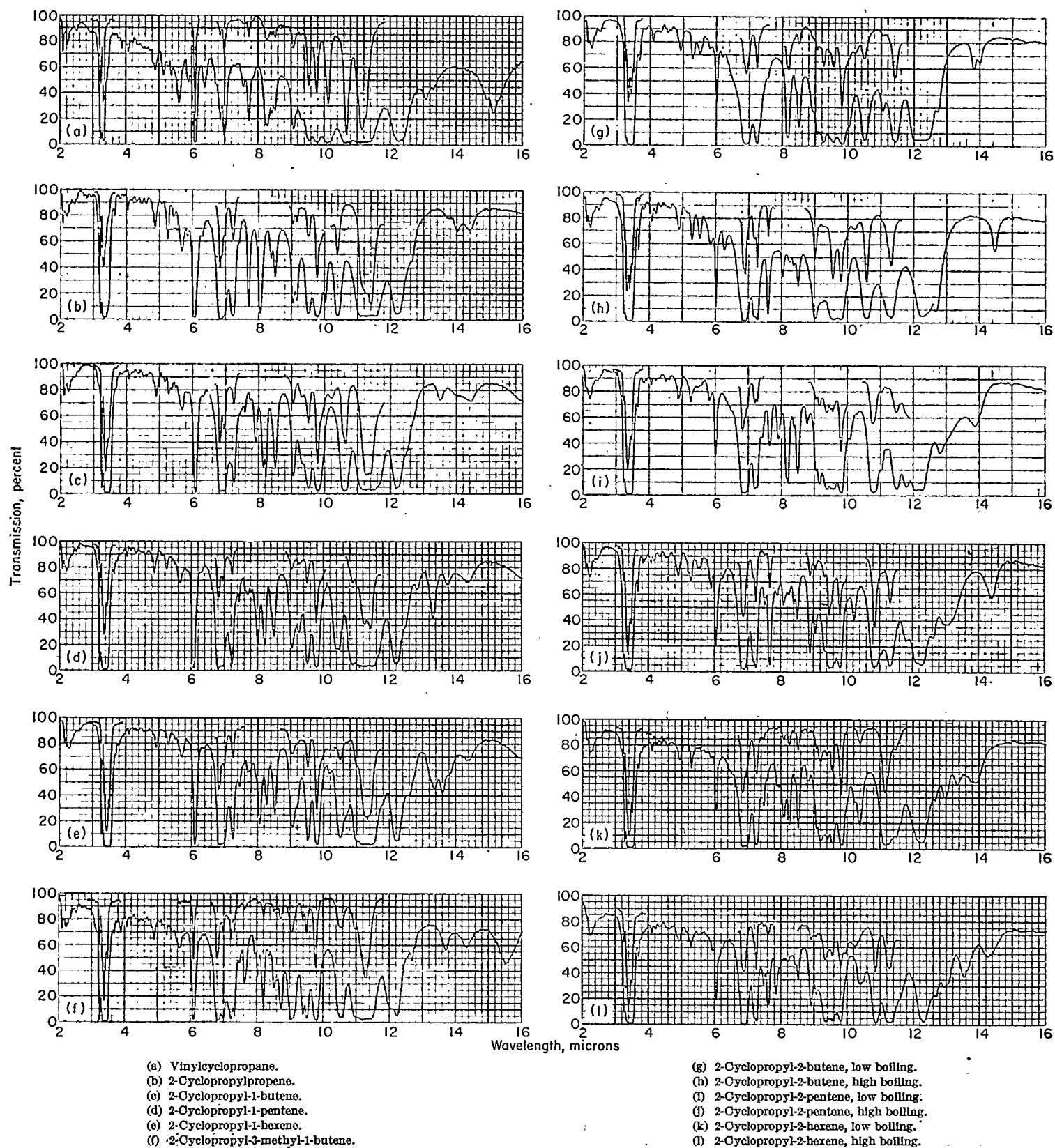


FIGURE 7.—Infrared spectra of cyclopropylalkenes. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

purities between 98 and 99 percent, whereas the hydrogenation of the 2-cyclopropyl-2-alkenes yields also significant quantities of paraffinic hydrocarbons. The paraffinic hydrocarbons do not appear to result from hydrogenolysis of the cyclopropyl ring, because if this were the case, larger amounts

of the paraffinic hydrocarbons would be obtained also from the hydrogenations of the 2-cyclopropyl-1-alkenes. The data support the proposal made in reference 28 that systems in which a cyclopropyl ring is conjugated with a double bond can add hydrogen by either a 1,2- or a 1,4-mechanism.

Purification of the 2-cyclopropylalkanes was difficult in those experiments in which methylalkanes were formed, because the boiling points of the paraffinic hydrocarbons

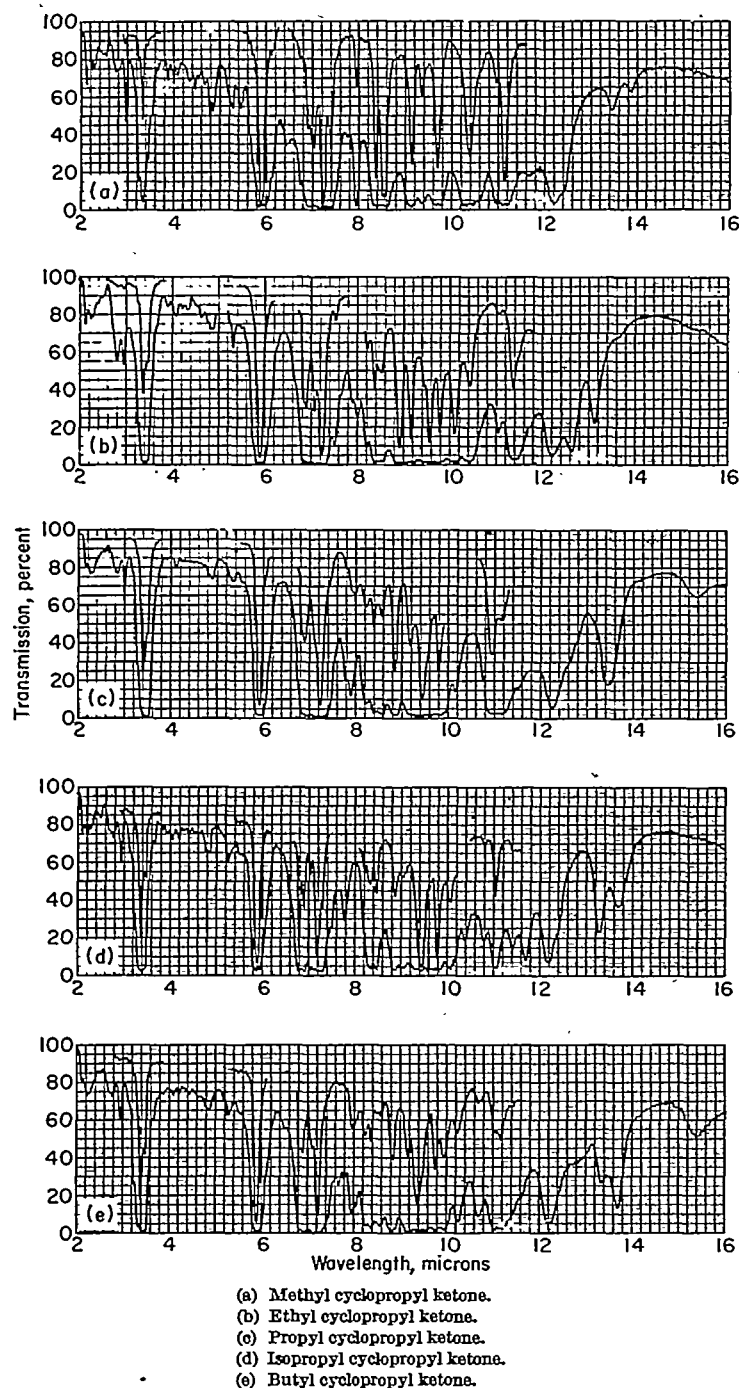


FIGURE 8.—Infrared spectra of alkyl cyclopropyl ketones. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

were within 2° C of the corresponding cyclopropylalkanes. Azeotropic fractionations with appropriate entrainers were found to be effective for separating the close-boiling mixtures. Pertinent data for the azeotropic mixtures are given in the following table:

Cyclopropylalkane	n_{D}^{20}	Entrainer	n_{D}^{20}	Azeotrope	
				n_{D}^{20}	Boiling point, $^{\circ}$ C
2-Cyclopropylbutane.....	1.4024	Ethanol.....	1.3614	1.3862	70
2-Cyclopropylpentane.....	1.4112	Propanol.....	1.3851	1.3973	63
2-Cyclopropylhexane.....	1.4178	Cellosolve.....	1.4079	1.4117	129
2-Cyclopropylhexane.....	1.4178	Butanol.....	1.3992	1.4056	116
2-Cyclopropyl-3-methylbutane.....	1.4140	Propanol.....	1.3851	1.3999	92

Purifications of the 2-cyclopropylalkanes were considered complete when (a) the melting curves of selected samples were interpreted to be indicative of purities of better than

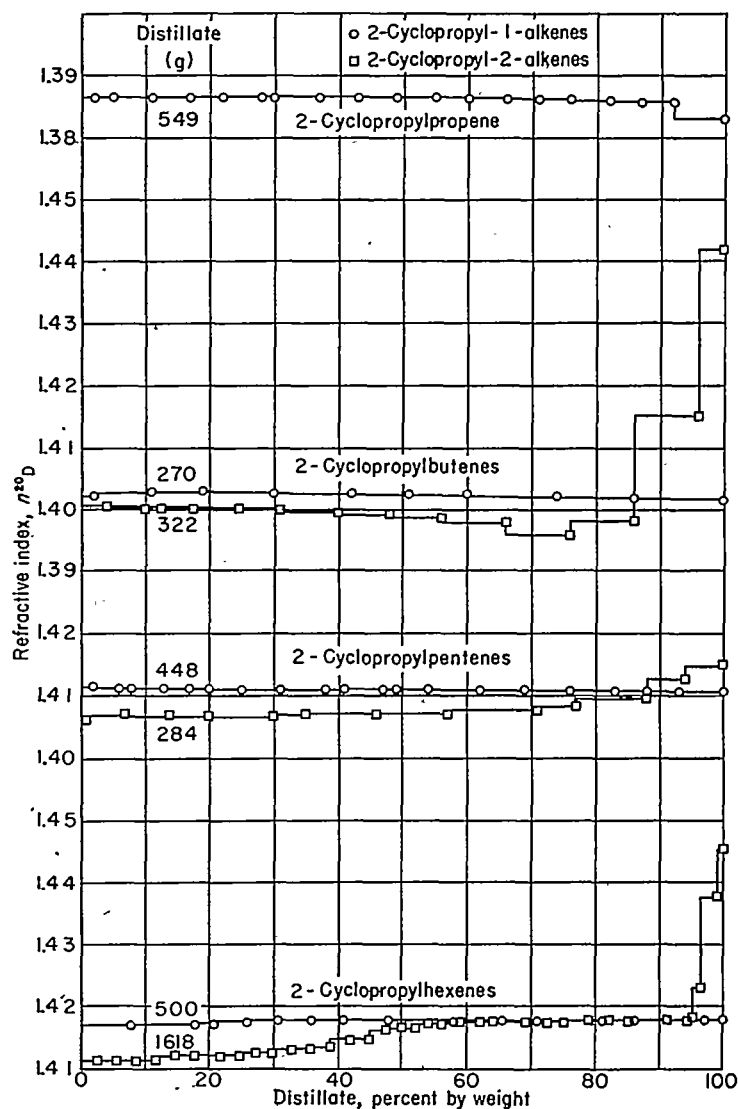


FIGURE 9.—Distillation of products from hydrogenations of 2-cyclopropylalkanes.

99 mole percent, or (b) repeated fractionations and azeotropic fractionations through columns rated at better than 150 theoretical plates gave no significant changes in refractive index and density of the hydrocarbons.

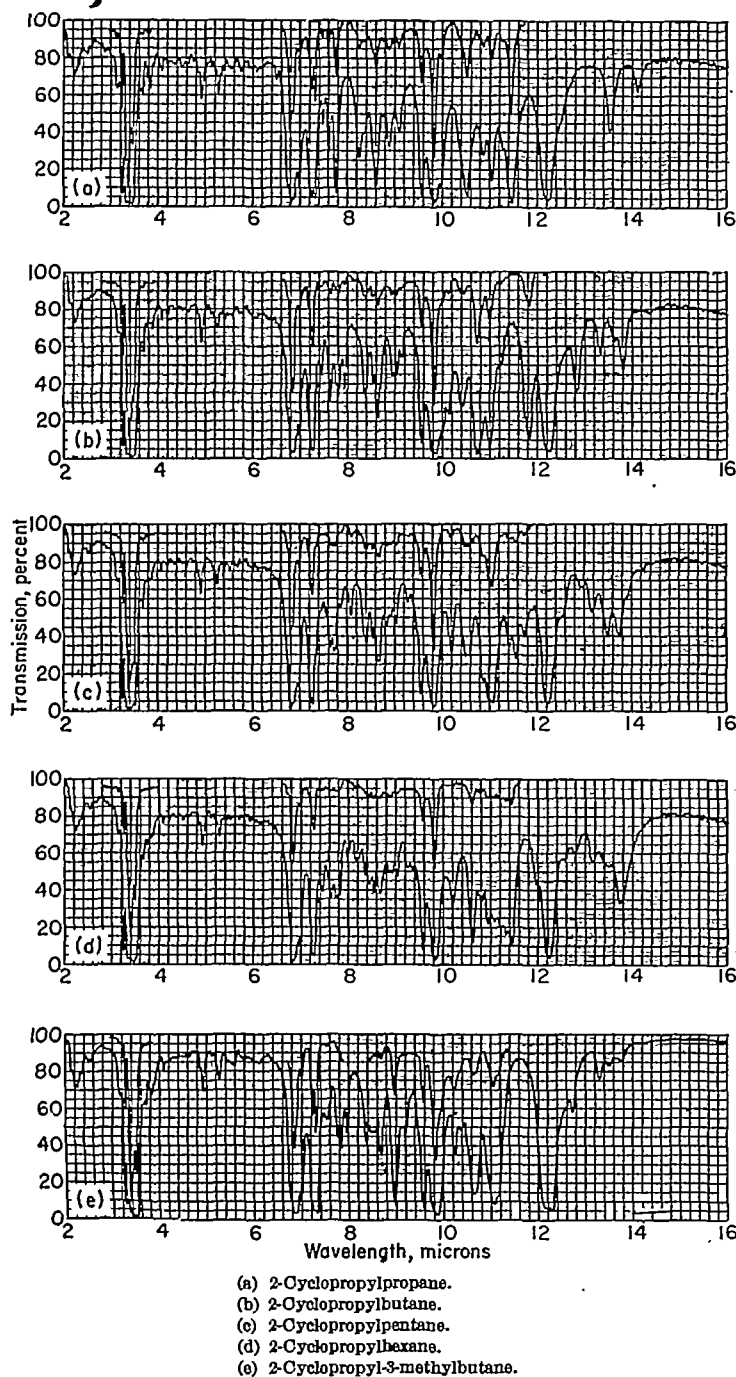


FIGURE 10.—Infrared spectra of 2-cyclopropylalkanes. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

The physical properties of the 2-cyclopropylalkanes are presented in the following table; previously reported properties are also referenced.

Although the purities of only two of the 2-cyclopropylalkanes could be calculated, it is believed that the other three hydrocarbons are of similar purities.

The infrared spectra of the 2-cyclopropylalkanes are shown in figure 10. All the spectra show characteristic cyclopropyl ring absorption at 9.82 microns.

2-Cyclopropylalkane	Melting point, °C	Melting point for zero impurity, °C	Change in melting point per mole percent of impurity, °C	Estimated purity, mole percent	Boiling point at 760 mm Hg, °C	n_D^{20}	d_4^{20} , g/ml	Net heat of combustion, kcal/mole
-propane--- Ref. 28---	-112.97 -118.3	^a -112.93 -115.24	^b 0.28 .20	99.9 85	58.31 58.7	1.3865 1.3853	0.69853 .6889	900
-butane---	Glass				90.08	1.4024	.72830	1,045
-pentane---	-118.46	(c)			117.74	1.4111	.74294	1,200
-hexane---	-93.04	^a -97.99	^d .20	99.7	142.95	1.4178	.76438	1,350
-3-methylbutane	Glass				115.49	1.4140	.75026	1,200

^a Determined by geometrical method of reference 41.

^b Determined by adding known amounts of 2-methylpentane.

^c Melting curve was not of sufficient duration to make calculation valid.

^d Determined by adding known amounts of 4-methyloctane.

CYCLOPROPYL CHLORIDES

Cyclopropyl chloride, 1,1-dichlorocyclopropane, and *trans*-1,2-dichlorocyclopropane were isolated from the reaction products of the photochemical chlorination of cyclopropane. A sketch of the photochlorination apparatus is shown in figure 2. In a typical reaction the source of illumination (two sun lamps) was placed 11.5 centimeters from the reaction chamber and the cyclopropane was passed through the reaction chamber at a rate of about 0.12 mole per minute. Chlorine was then added at a rate of about 0.046 mole per minute. The gases were passed through the reaction chamber simultaneously for 6 hours, and at the end of this period the amount of cyclopropane used was 44.4 moles (1866 g), and the amount of chlorine 16.2 moles (1148 g). The excess cyclopropane was distilled from the products, and the products were then combined with the products from eleven similar chlorination experiments. Distillation of the combined products gave the data plotted in figure 11.

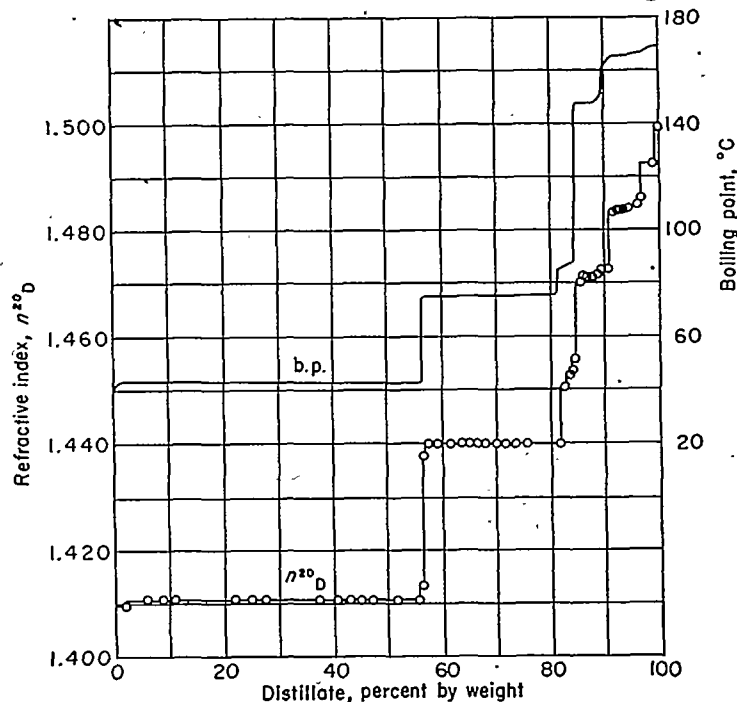


FIGURE 11.—Distillation of products from photochlorination of cyclopropane. Total distillate, 8155 grams; residue, 615 grams.

From these data and subsequent fractional distillation data, the following composition of the chlorination products was estimated: 52 weight percent cyclopropyl chloride, 24 weight percent 1,1-dichlorocyclopropane, 2 weight percent *trans*-1,2-dichlorocyclopropane, 2 weight percent of a compound believed from its physical properties to be 1,1,3-trichloropropane, and 20 weight percent of a complex mixture of polyhalides which could not be separated by fractional distillation.

The cyclopropyl halides were purified by refractionation at efficiencies of 50 to 60 theoretical plates. The physical properties of the purified halides are compared in the following table with those values previously reported:

Cyclopropyl halide	Melting point, °C	Boiling point at 760 mm Hg, °C	n_D^{25}	d_4^{20} , g/ml
Cyclopropyl chloride..... (ref. 42)	^a -97.68	43.43	1.4108	0.9962
1,1-Dichlorocyclopropane..... (ref. 43)	^a -37.47	43	^b 1.4079	^b 1.9899
<i>trans</i> -1,2-Dichlorocyclopropane..... (ref. 43)	-18.74	75.55	1.4400	1.2158
	-19.5	75.0	^b 1.4377	^b 1.2178
		87.94	1.4626	1.2459
		87.2	^b 1.4602	^b 1.2492

^a Freezing point, °C.

^b At 25° C.

The infrared spectra of the three chlorinated cyclopropanes are shown in figure 12; the absorption band characteristic of

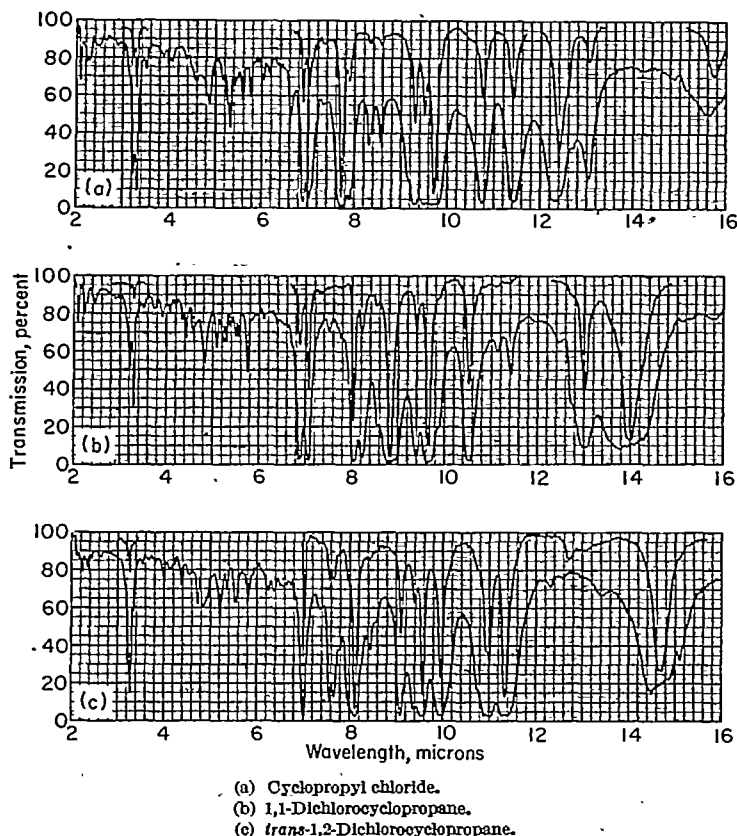


FIGURE 12.—Infrared spectra of cyclopropyl chlorides. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon disulfide; lower trace, undiluted.

the cyclopropyl ring is seen to shift from 9.73 microns (cyclopropyl chloride) to 9.66 microns (1,1-dichlorocyclopropane) as the number of chlorine atoms is increased. The absorption shifts to even lower frequency when the two

chlorine atoms are on different carbon atoms (9.58 microns in *trans*-1,2-dichlorocyclopropane).

DICYCLOPROPYL

The reaction of cyclopropyl chloride with lithium or sodium was used to prepare dicyclopropyl. The reaction was tried with lithium both in methyleyclohexane and in ether, and with sodium in ether. In general, the chloride was dissolved in the reaction solvent and added to a suspension of the metal in the solvent contained in a flask equipped with a stirrer, a reflux condenser, and an addition funnel. All reactions were carried out at 25° to 35° C. Other reaction conditions and yields of products are summarized in the following table (ref. 38):

Chloride, moles	Alkali metal	Metal, gram-atoms	Solvent	Reaction time, days	Yields of products, percent	
					Cyclopropane	Dicyclopropyl
2	Sodium	2	Ether	5	40	10
20		20	do	10	42	12
4		4	Methyleyclohexane	7	None	None

These data indicate that the reaction with sodium or lithium in ether gives approximately the same yields of the two products listed in the table. The fact that no reaction was obtained in methyleyclohexane solution clearly indicates that the solvent in some manner influences the course of the reaction.

Although cyclopropane and dicyclopropyl were the principal reaction products, trace quantities of two other hydrocarbons were detected in the crude reaction product by means of infrared spectra. The infrared evidence indicated that one of these hydrocarbons was 1-hexyne; the other was not identified.

Dicyclopropyl was purified by extracting the hydrocarbon with an ice-cold saturated solution of silver nitrate to remove the unsaturated impurities, passing the extracted hydrocarbon through silica gel, and, finally, azeotropically fractionating the hydrocarbon with ethanol through a Podbielniak column. The purified hydrocarbon had the following physical properties:

Melting point, °C.....	-82.62
Boiling point at 760 mm Hg, °C.....	76.10
Refractive index, n_D^{20}	1.4239
Density, g/ml.....	0.78979
Net heat of combustion, kcal/mole.....	885

The infrared spectrum of dicyclopropyl, shown in figure 13, has a strong absorption band at 9.82 microns, which is characteristic of the cyclopropyl ring.

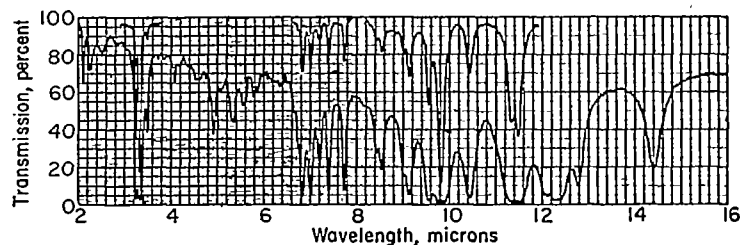


FIGURE 13.—Infrared spectrum of dicyclopropyl. Liquid phase; 0.1-millimeter cell. Upper trace diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

SPIROPENTANE

Spiropentane was prepared by the debromination of pentaerythrityl tetrabromide (ref. 44) with zinc dust in the presence of sodium carbonate and sodium iodide. The reaction was conducted by adding small portions of the powdered tetrabromide to a slurry of the zinc dust, sodium carbonate, and sodium iodide either in molten acetamide or in 75 percent ethanol (ref. 39). The hydrocarbon product was distilled from the reaction mixture as it formed, and was collected in receivers chilled with a mixture of solid carbon dioxide and acetone. In addition to spiropentane, two other hydrocarbons were obtained from the reaction, namely, methylenecyclobutane and 2-methyl-1-butene. Some typical experiments are summarized in the following table (ref. 39):

Solvent	Reactants, moles				Yields of products, percent		
	Pentaerythrityl tetrabromide	Zinc	Sodium carbonate	Sodium iodide	Spiropentane	Methylenecyclobutane	2-Methyl-1-butene
Ethanol.....	5	20	5	0.83	21	43	12
Do.....	5	20	5	.83	22	44	12
Acetamide.....	1	6	1.2	.16	22	4	11

These data indicate that the reduction in either solvent gives nearly identical yields of spiropentane, but that the reduction in ethanol gives ten times the quantity of methylenecyclobutane as the reduction in acetamide. For preparations of sufficient size so that precise fractional distillations can be employed to separate the products, reduction in ethanol is the preferable method, especially if methylenecyclobutane as well as spiropentane is desired. For small preparations of spiropentane, the reduction in acetamide may be more suitable (ref. 45).

The physical properties of spiropentane are given in the following table with those values previously obtained:

Hydrocarbon	Freezing point, °C	Boiling point*		n_D^{20}	d_4^{20} , g/ml
		Temperature, °C	Pressure, mm Hg		
Spiropentane.....	-107.05	38.84	760	1.4122	0.7551
Ref. 45.....	-----	38.3-38.5	760	1.4117	.755

The infrared spectrum of spiropentane is shown in figure 14. The absorption band characteristic of the cyclopropyl ring is located at 9.54 microns, a shorter wavelength than in

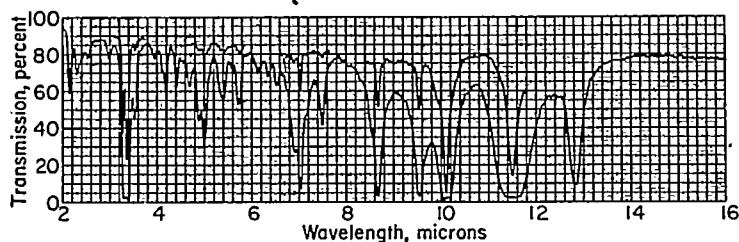


FIGURE 14.—Infrared spectrum of spiropentane. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

any of the other compounds prepared in the present investigation. Such a shift in the absorption is not entirely unexpected, because the force constants in the spiro structure would be different from those in the other cyclopropanes.

DIETHYL CYCLOPROPANE-1,1-DICARBOXYLATE

The diethyl cyclopropane-1,1-dicarboxylate was prepared by the method of reference 46 in which a solution of sodium ethoxide, obtained by dissolving 365 grams (16.5 g-atoms) of sodium metal in 5500 milliliters of absolute ethanol, was added dropwise to a mixture of 1275 grams (8 moles) of ethyl malonate and 1550 grams (7.2 moles) of ethylene bromide. The products of the reaction were distilled at 10 millimeters of mercury pressure, and the material boiling between 80° and 120° C was collected for subsequent fractionation at about 50 theoretical plate efficiency at atmospheric pressure. The yield of diethyl cyclopropane-1,1-dicarboxylate was 495 grams (33 percent). Several fractions of constant refractive index were combined and passed through silica gel in order to obtain the sample used for the determination of physical properties and infrared spectrum. The physical properties are compared in the following table with values previously reported:

	Melting point, °C	Boiling point		n_D^{20}	d_4^{20} , g/ml
		Temperature, °C	Pressure, mm Hg		
Diethyl cyclopropane-1,1-dicarboxylate.	-47.05	217.4	760	1.4340	1.0595
Ref. 47.....	-----	114	22	1.43310	1.0615

The infrared spectrum of diethyl cyclopropane-1,1-dicarboxylate is shown in figure 15; strong absorption is

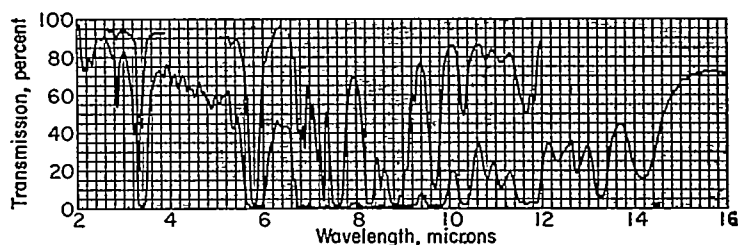


FIGURE 15.—Infrared spectrum of diethylcyclopropane-1,1-dicarboxylate. Liquid phase; 0.1-millimeter cell. Upper trace, diluted 1:10 with carbon tetrachloride; lower trace, undiluted.

observed at 5.8 microns, the region in which carbonyl groups absorb strongly, and also at 9.70 microns. The 9.70-micron band is undoubtedly that band characteristic of the cyclopropyl ring.

INFRARED ABSORPTION CHARACTERISTIC OF CYCLOPROPYL RING

The difficulty in establishing the presence of the cyclopropyl ring in organic molecules by chemical means has promoted interest in identifying the presence of the ring by infrared techniques. Infrared absorption bands in three regions of the spectrum have been proposed to offer a means of identifying the cyclopropyl ring. In reference 4 bands at 9.75 and 11.55 microns were employed. The authors of reference 48 found that in the spectra of 14 cyclopropane

hydrocarbons a strong band was present between 9.8 and 10.0 microns, but that strong absorption did not occur consistently at 11.6 microns. It was reported recently in reference 49 that a study of the 3- to 4-micron region with a lithium fluoride prism disclosed that all the cyclopropane derivatives investigated had absorption bands at 3.23 and 3.32 microns which were characteristic of the C-H vibrations of the cyclopropyl ring system.

The infrared spectra of the 34 cyclopropane derivatives reported herein have been examined in each of the three regions proposed previously. Unfortunately, a critical examination of the 3- to 4-micron region could not be made in the present work, because the sodium chloride prism, employed in determining the spectra, does not give sufficient resolution to separate both the 3.23- and 3.32-micron cyclopropyl ring C-H bands from other carbon-hydrogen bands in this region. An examination of the spectra of the diluted samples does disclose that many of the cyclopropane derivatives have bands at 3.23 ± 0.02 microns and at 3.33 ± 0.02 microns. In compounds such as vinylcyclopropane, dicyclopropyl, cyclopropyl chloride, and spiro-pentane, in which there is little interference from carbon-hydrogen bands other than those of the ring, the 3.23- and 3.32-micron bands show up clearly (table I).

Nearly all the cyclopropane derivatives show strong absorption between 11 and 12 microns; however, the position of the absorption which might be characteristic of the cyclopropyl ring is difficult to determine because of the broadness of the absorption. Interfering absorption from certain olefinic structures also occurs in this region.

The absorption which appears to be most promising for determining the presence of the cyclopropyl ring is that used in reference 48. In the spectra of all the cyclopropane compounds prepared in the present investigation, a strong band was observed at 9.7 to 9.8 microns (table II). In only a few instances was the band shifted appreciably from this region, and in these instances, for example, in spiro-pentane and in *trans*-1,2-dichlorocyclopropane, the shift in absorption is not entirely unexpected. Not only is the absorption strong in the undiluted spectra, but it is persistent also upon dilution.

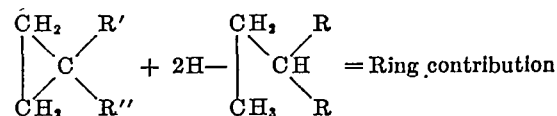
MOLECULAR REFRACTION OF CYCLOPROPANE DERIVATIVES

The experimentally observed molecular refractions of cyclopropane compounds are generally higher than those calculated from the atomic and group refractivities. This difference in observed and calculated values was interpreted by Tschugaeff (ref. 50) to result from a contribution to the refraction by the three-carbon ring structure. From a comparison of observed and calculated refractions of three cyclopropane derivatives and several bicyclic terpenes which had three-carbon rings in their structures, Tschugaeff estimated the magnitude of the ring contribution to be about 0.7. A more comprehensive investigation by Östling (ref. 51) yielded a value which agreed well with that of reference 50. Subsequent investigations, however, showed that the difference between observed and calculated molec-

ular refractions varied considerably among different classes of cyclopropane derivatives and even among members of the same class (refs. 26, 27, and 52). Data obtained in the present work (table III) also showed this variation in ΔM_R .

The lack of agreement among the ΔM_R values from various classes of cyclopropane derivatives and even among members of an homologous series is not surprising. It must be assumed in determining ring contribution by this procedure that the atomic and group refractivities are truly constant and additive. Atomic and group refractivities, however, are constant and additive only within limitations (ref. 53), and as the character of the atoms or groups in the structure is varied, the atomic and group refractivities also vary. Consequently, ΔM_R reflects not only ring contribution, but also deviations from constancy of the atomic and group refractivities used to determine the calculated molecular refractions.

In a recent investigation, Jeffery and Vogel (ref. 47) employed a procedure for determining ring contribution that reduces the effect of inconstancy of atomic and group refractivities. The observed molecular refraction of a structurally similar acyclic compound is subtracted from the sum of the observed molecular refraction of the cyclopropane compound and two hydrogen atomic refractivities:



From data obtained principally with alkyl cyclopropane mono- and dicarboxylates, the ring contribution to the molecular refraction was calculated to be 0.614 (ref. 47).

Vogel's procedure has been used in the present work to determine the ring contribution in the cyclopropylalkanes and in some of the cyclopropylalkenes (table IV). A nearly constant value for ring contribution among the cyclopropylalkanes is obtained by this procedure in contrast to the inconstant ΔM_R in table III for the same compounds. Although Vogel's procedure minimizes the effect of environment on the atomic refractivities of carbon and hydrogen, the discrepancy between the ring contribution obtained with the cyclopropylalkanes and that obtained with the cyclopropane carboxylates, 0.44 and 0.614, respectively, indicates that the nature of the ring substituents also influences the ring contribution. While it may be said that the compounds used by Vogel are capable of conjugation between the cyclopropyl ring and the carbonyl double bond, and that the value 0.614 includes exaltation due to conjugation, nevertheless, environmental factors influence the combined effects of ring contribution and conjugation as indicated by the data in table IV for the cyclopropylalkenes, methyl cyclopropyl ketone, and diethyl cyclopropane-1,1-dicarboxylate.

Because of the varying influence of the substituent group on the cyclopropyl ring, it is doubtful that any of the proposed values will adequately express for all structures the contribution of the cyclopropyl ring to the molecular refraction. The calculation of molecular refraction of cyclopropane derivatives can, therefore, at best give only an approximation of the observed refraction.

CONCLUDING REMARKS

The methods of synthesizing and purifying 34 hydrocarbon and nonhydrocarbon derivatives of cyclopropane were discussed, and the physical properties and the infrared spectra of each of the compounds were presented.

It was found that a series of cyclopropylalkenes could be prepared by dehydrating appropriate alkyl- or methylalkyl-cyclopropylcarbinols, either with concentrated sulfuric acid or with alumina at temperatures between 200° and 300° C. Furthermore, in the presence of a barium-promoted copper chromite catalyst, the cyclopropylalkenes were catalytically hydrogenated to the corresponding cyclopropylalkanes. The position of the double bond was found to greatly influence both the ease of hydrogenation and the yield of products. The cyclopropyl-1-alkenes hydrogenated readily at 100° C to give the corresponding cyclopropylalkane and only 1 to 2 percent of paraffinic product, whereas the cyclopropyl-2-alkenes hydrogenated sluggishly even at higher temperatures to give 15 to 17 percent of paraffinic product in addition to the cyclopropylalkanes. In the hydrogenation experiments, additional evidence was found to support the proposal that conjugated cyclopropylalkenes can add hydrogen by both a 1,2- and a 1,4-mechanism.

Dicyclopentyl, the smallest of the dicyclic hydrocarbons, was prepared for the first time. Spiropentane, the smallest of the spiro hydrocarbons, was also prepared.

Infrared absorption bands characteristic of the cyclopropyl ring were discussed, and some observations were made on the contribution of the cyclopropyl ring to the molecular refractions of cyclopropane derivatives.

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CLEVELAND, OHIO, August 15, 1952

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$$\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{C} \begin{array}{l} \nearrow \text{CH-R} \\ \searrow \end{array} \\ | \\ \text{H}_2\text{C} \end{array}$$

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TABLE I.—CARBON-HYDROGEN ABSORPTION BANDS IN INFRARED SPECTRA OF CYCLOPROPANE DERIVATIVES

Cyclopropane derivatives	Wavelength, microns						
	3.21-3.25	3.26-3.30	3.31-3.35	3.36-3.40	3.41-3.45	3.46-3.50	3.51-3.55
2-Cyclopropylpropane.....	3.24	-----	3.32s	3.37	-----	3.48	-----
2-Cyclopropylbutane.....	3.25	-----	-----	3.38	3.42s	3.48	-----
2-Cyclopropylpentane.....	3.25	-----	-----	3.38	3.42s	3.49	-----
2-Cyclopropylhexane.....	-----	3.26	-----	3.38	3.42s	3.49	-----
2-Cyclopropyl-3-methylbutane.....	-----	3.26	-----	3.40	3.43s	-----	3.51
Vinylcyclopropane.....	3.25	-----	3.32	-----	-----	-----	-----
2-Cyclopropylpropane.....	3.22	3.30	-----	3.38s	-----	3.47s	-----
2-Cyclopropyl-1-butene.....	3.25	-----	3.33s	3.37	3.42s	3.48s	-----
2-Cyclopropyl-1-pentene.....	3.22	* 3.30s	-----	3.37	3.45	-----	-----
2-Cyclopropyl-1-hexene.....	-----	3.27	3.35s	-----	3.44	-----	3.52
2-Cyclopropyl-3-methyl-1-butene.....	3.24	-----	3.33s	3.37	3.41s	3.48	-----
2-Cyclopropyl-2-butene (l. b.).....	3.25	-----	3.34	-----	3.43	3.49	-----
2-Cyclopropyl-2-pentene (l. b.).....	3.24	-----	3.35	-----	-----	3.47	-----
2-Cyclopropyl-2-hexene (l. b.).....	3.25	-----	3.34s	3.39	3.43s	-----	3.52
2-Cyclopropyl-2-butene (h. b.).....	3.24	-----	3.32	-----	3.41	3.49	-----
2-Cyclopropyl-2-pentene (h. b.).....	3.24	-----	-----	3.37	-----	3.48	-----
2-Cyclopropyl-2-hexene (h. b.).....	-----	3.27	-----	3.40	-----	-----	3.51
Spiropropane.....	-----	3.28	-----	3.36	-----	-----	3.53
Dicyclopropyl.....	3.24	-----	3.33	3.40	-----	3.49	-----
Methylcyclopropylcarbinol.....	3.25	-----	-----	3.37	-----	3.48	-----
Dimethylcyclopropylcarbinol.....	-----	3.30	-----	-----	3.42	3.50s	-----
Methylethylcyclopropylcarbinol.....	3.25	-----	-----	3.37	3.42s	-----	-----
Methylpropylcyclopropylcarbinol.....	-----	3.27	-----	3.40	-----	-----	-----
Methylbutylcyclopropylcarbinol.....	-----	3.27	-----	-----	3.42	-----	3.52
Methylisopropylcyclopropylcarbinol.....	-----	3.28	-----	-----	3.41	3.50s	-----
Cyclopropyl chloride.....	3.23	-----	3.32	-----	-----	-----	-----
1, 1-Dichlorocyclopropane.....	3.21	3.29	-----	-----	-----	-----	-----
trans-1, 2-Dichlorocyclopropane.....	3.25s	3.27	3.34s	-----	-----	-----	-----
Methyl cyclopropyl ketone.....	3.24	-----	3.34	3.38	3.44s	-----	-----
Ethyl cyclopropyl ketone.....	-----	3.26s	-----	3.36	3.43s	3.48s	-----
Propyl cyclopropyl ketone.....	-----	-----	-----	3.40	-----	-----	3.51s
Butyl cyclopropyl ketone.....	3.24	-----	3.32	3.38	-----	3.48	-----
Isopropyl cyclopropyl ketone.....	3.22	-----	-----	3.36, 3.40	-----	3.48	-----
Diethyl cyclopropane-1, 1-dicarboxylate.....	-----	-----	3.33	3.38s	3.42	-----	-----

* The symbol s denotes band which shows only as a shoulder on a stronger absorption.

TABLE II.—CHARACTERISTIC ABSORPTION IN INFRARED FOR CYCLOPROPYL RING

Cyclopropane derivative	Wavelength, microns
2-Cyclopropylpropane.....	9.82
2-Cyclopropylbutane.....	9.82
2-Cyclopropylpentane.....	9.82
2-Cyclopropylhexane.....	9.82
2-Cyclopropyl-3-methylbutane.....	9.83
Vinylcyclopropane.....	9.77
2-Cyclopropylpropene.....	9.77
2-Cyclopropyl-1-butene.....	9.78
2-Cyclopropyl-1-pentene.....	9.78
2-Cyclopropyl-1-hexene.....	9.79
2-Cyclopropyl-3-methyl-1-butene.....	9.78
2-Cyclopropyl-2-butene (l. b.).....	9.82
2-Cyclopropyl-2-pentene (l. b.).....	9.80
2-Cyclopropyl-2-hexene (l. b.).....	9.82
2-Cyclopropyl-2-butene (h. b.).....	9.80
2-Cyclopropyl-2-pentene (h. b.).....	9.80
2-Cyclopropyl-2-hexene (h. b.).....	9.80
Spiropentane.....	9.54
Dicyclopropyl.....	9.82
Methylcyclopropylcarbinol.....	9.75
Dimethylcyclopropylcarbinol.....	9.78
Methylethylcyclopropylcarbinol.....	9.77
Methylpropylcyclopropylcarbinol.....	9.78
Methylbutylcyclopropylcarbinol.....	9.80
Methylisopropylcyclopropylcarbinol.....	9.75
Cyclopropyl chloride.....	9.73
1,1-Dichlorocyclopropane.....	9.66
trans-1,2-Dichlorocyclopropane.....	9.53
Methyl cyclopropyl ketone.....	9.69
Ethyl cyclopropyl ketone.....	9.78
Propyl cyclopropyl ketone.....	9.80
Butyl cyclopropyl ketone.....	9.75
Isopropyl cyclopropyl ketone.....	9.78
Diethyl cyclopropane-1,1-dicarboxylate.....	9.70

TABLE III.—MOLECULAR REFRACTIONS OF CYCLOPROPANE DERIVATIVES

Cyclopropane derivative	M_R^b (calc.)	M_R^b (obs.)	ΔM_R
2-Cyclopropylpropane.....	27.88	28.33	0.45
2-Cyclopropylbutane.....	32.53	32.85	.32
2-Cyclopropylpentane.....	37.18	37.51	.33
2-Cyclopropylhexane.....	41.82	42.15	.33
2-Cyclopropyl-3-methylbutane.....	37.18	37.37	.19
Vinylcyclopropane.....	22.75	23.60	0.85
2-Cyclopropylpropene.....	27.40	27.98	.58
2-Cyclopropyl-1-butene.....	32.05	32.46	.41
2-Cyclopropyl-1-pentene.....	36.70	37.12	.42
2-Cyclopropyl-1-hexene.....	41.34	41.75	.41
2-Cyclopropyl-3-methyl-1-butene.....	36.70	37.06	.36
2-Cyclopropyl-2-butene (l. b.).....	32.05	32.63	0.58
2-Cyclopropyl-2-pentene (l. b.).....	36.70	37.47	.77
2-Cyclopropyl-2-hexene (l. b.).....	41.34	42.11	.77
2-Cyclopropyl-2-butene (h. b.).....	32.05	32.66	0.61
2-Cyclopropyl-2-pentene (h. b.).....	36.70	37.45	.75
2-Cyclopropyl-2-hexene (h. b.).....	41.34	42.13	.79
Spiropentane.....	21.18	22.45	1.27
Dicyclopropyl.....	25.83	26.63	.70
Methylcyclopropylcarbinol.....	24.75	25.12	0.37
Dimethylcyclopropylcarbinol.....	29.40	29.65	.25
Methylethylcyclopropylcarbinol.....	34.05	34.25	.20
Methylpropylcyclopropylcarbinol.....	38.69	38.85	.16
Methylbutylcyclopropylcarbinol.....	43.34	43.48	.14
Methylisopropylcyclopropylcarbinol.....	38.69	38.64	-.05
Cyclopropyl chloride.....	18.76	19.07	0.31
1,1-Dichlorocyclopropane.....	23.57	24.06	.49
trans-1,2-Dichlorocyclopropane.....	23.57	24.06	.49
Methyl cyclopropyl ketone.....	23.34	23.94	0.60
Diethyl cyclopropane-1,1-dicarboxylate.....	44.93	45.77	0.84

* Atomic and group refractivities of reference 54 were used.

 $\frac{n^2-1}{n^2+2} \times \frac{m}{d} = M_R$ (observed).

TABLE IV.—CONTRIBUTION OF CYCLOPROPYL RING TO MOLECULAR REFRACTION

$\text{Ring contribution} = \begin{array}{c} \text{CH}_2 \quad \text{R}' \\ \diagdown \quad \diagup \\ \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{R}'' \end{array} + 2\text{H} - \begin{array}{c} \text{CH}_2 \quad \text{R}' \\ \diagdown \quad \diagup \\ \text{OH} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{R}'' \end{array}$				
Cyclopropane derivatives	M_R (obs.)	Aliphatic compounds	M_R^b (obs.)	Ring contribution
2-Cyclopropylpropane.....	28.33	2-Methylpentane.....	29.95	0.44
2-Cyclopropylbutane.....	32.85	3-Methylhexane.....	34.47	.44
2-Cyclopropylpentane.....	37.51	4-Methylheptane.....	39.13	.45
2-Cyclopropyl-3-methylbutane.....	37.37	2, 3-Dimethylhexane.....	38.99	.44
2-Cyclopropylhexane.....	42.14	4-Methyloctane.....	43.77	.43
Dicyclopropyl.....	26.53	n-Hexane.....	29.91	.37
Vinylcyclopropane.....	23.60	1-Pentene.....	24.83	* 0.83
2-Cyclopropylpropene.....	27.98	2-Methyl-1-pentene.....	29.42	* .62
2-Cyclopropyl-1-butene.....	32.46	2-Ethyl-1-pentene.....	34.0	* .5
Methyl cyclopropyl ketone.....	23.94	Methyl propyl ketone.....	^d 25.25	* 0.75
Diethyl cyclopropane-1, 1-dicarboxylate.....	45.77	Diethyl ethylmalonate.....	* 47.07	* 0.77

* Atomic refraction for hydrogen taken from reference 54.

b From reference 55.

c Includes ring contribution plus any exaltation accompanying conjugation.

d From reference 56.

e From reference 57.